



Separation of nickel from cobalt using electrodialysis in the presence of EDTA

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Abstract

Optimum conditions are determined for the removal of nickel from cobalt solutions by electrodialysis exploiting the greater stability of the EDTA complex with nickel. The $\text{Ni}-(\text{EDTA})^{2-}$ complex and hydrated Co^{2+} ions are transferred from the feed solution to the electrodialysis anolyte and catholyte chambers, respectively. A three compartment cell is required to prevent the transfer of hydrated Ni^{2+} from the anolyte chamber as the EDTA present is destroyed at the anode. Complete removal of nickel from cobalt can be achieved but there is a compromise between cobalt purity and the percentage of cobalt transferred to the catholyte chamber for recovery.

1. Introduction

The separation of cobalt and nickel is difficult because of the similarities in their properties. The methods in use also tend to be more efficient in removing cobalt from nickel than for nickel from cobalt and most are based on differences in the solubilities or the kinetic or thermodynamic stabilities of their chemical compounds. Methods used [1] include those exploiting small differences in the behaviour of the hydroxides, oxides, carbonates, amine complexes, double ammonium salts, sulphides, chlorides, carbonyls and sulphites of the metals and in differences in the rates of cementation of the dissolved metal ions when reduced with hydrogen or other metals such as zinc. The physio-chemical separation methods used include ion exchange [2], solvent extraction [3], liquid membrane technology [4] and electrodialysis in the presence of complexing agents [5]. The use of electrodialysis for separation of cobalt and nickel has been achieved using ion exchange membranes in the presence of EDTA exploiting a difference in the solubility constants of the $\text{Ni}-\text{EDTA}$ ($10^{-18.6}$) and $\text{Co}-\text{EDTA}$ ($10^{-16.2}$) complexes but the method has not been optimized for the removal of nickel from cobalt solutions. Other separations have been achieved by electrodialysis in the presence of EDTA including Ca from Cd [6]; Ag from Zn and Cu [7] Na from Ca [8].

We now report on the optimization of an electrodialysis process for the separation of nickel impurities from cobalt solution.

2. Experimental details

Two types of electrodialysis cell were used, namely, a two compartment and a three compartment cell both with titanium mesh anodes coated with mixed metal oxide and stainless steel mesh cathodes. Cobalt and nickel solutions were prepared from reagent grade cobalt(II) sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) and reagent grade nickel(II) sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$). Ethylenediaminetetraacetic acid (EDTA) was used either as the free acid or as the disodium salt. A current density of 8.3 A m^{-2} was applied unless otherwise stated and the voltage was kept at a maximum. The purification of cobalt resulting from the separation of nickel was calculated from the Co:Ni ratio in the catholyte chamber and the purification of nickel was calculated from the Ni:Co ratio in the anolyte chamber. Experiments were carried in replicate and are reproducible.

2.1. Electrodialysis using a two-compartment cell

This cell (Figure 1(a)) consisted of two 400 cm^3 compartments, an anolyte chamber and a catholyte chamber, separated by a Nafion[®] cation exchange membrane (C), with a gap of 1.5 cm between each electrode and the membrane. The initial anolyte solutions were mixtures of Ni^{2+} and Co^{2+} ions (500 mg dm^{-3} for each) in 0.01 mol dm^{-3} sulphuric acid containing EDTA while the initial catholyte solution was 0.01 mol dm^{-3} sulphuric acid. Small quantities of H_2SO_4 were added to the catholyte chamber when

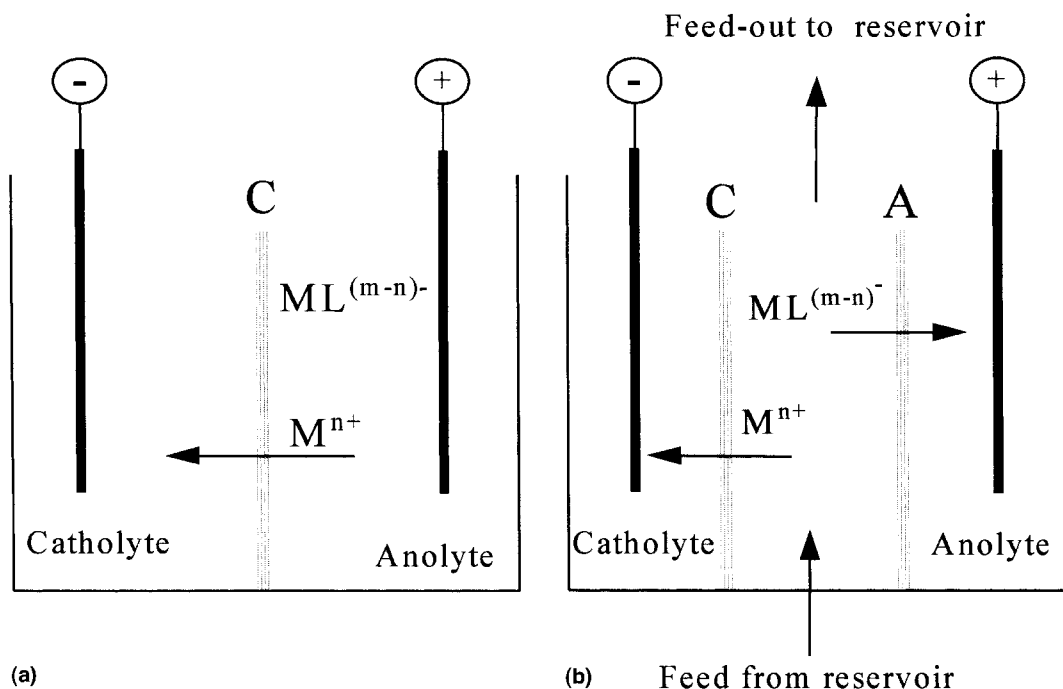


Fig. 1. Electrodialysis cell: (a) with two compartments and (b) with three compartments.

required during the electrolysis process to prevent the formation of metal hydroxide precipitates. The effects of pH, concentration of EDTA as free acid and disodium salt and Co:Ni ratio on the separation were studied.

2.2. Electrodialysis using a three-compartment cell

This cell (Figure 1(b)) consisted of two 400 cm³ compartments, namely, a catholyte chamber and an anolyte chamber separated by a 100 cm³ feed compartment between Nafion® cation (C) and ADP Solvay anion exchange (A) membranes in the sequence, anode: anion exchange membrane: feed compartment: cation exchange membrane: cathode. 0.01 mol dm⁻³ H₂SO₄ was the initial electrolyte in the anolyte and catholyte chambers and the initial feed solution consisted of nickel and cobalt ions in 0.01 mol dm⁻³ H₂SO₄ in the presence of the complexing agent EDTA as the disodium salt. The feed compartment is fed by circulating the Co–Ni solution through the feed compartment from a 400 cm³ reservoir. Small quantities of H₂SO₄ were added to the catholyte chamber when required during the electrolysis process to prevent the formation of cobalt hydroxide precipitates. The effects of the following variables on the separation of nickel from cobalt were studied; EDTA concentration, current, initial Co:Ni ratio and H₂SO₄ concentration.

The transfer and fate of EDTA in the electrodialysis process was also followed in the three compartment cell by HPLC using a 12.5 cm × 4.5 mm o.d. separation column packed with a polystyrene divinylbenzene copolymer (PLRP-S5). EDTA was eluted from the column in a 25:75 acetonitrile:water system containing 3 g dm⁻³

tetrabutylammonium bromide at pH 6.0 and analysed by monitoring the absorbance at 300 nm.

3. Results and discussion

3.1. Study of a two-compartment cell

A two-compartment cell was used to determine whether nickel separation from cobalt can be achieved using a cation exchange membrane. The results (Table 1) obtained from a two-compartment cell showed that very little separation could be achieved using a single cation exchange membrane. Although the Ni–EDTA complex is formed preferentially and should not be transferred through the cation exchange membrane, the fact that EDTA is destroyed at the anode surface, means that uncomplexed Ni²⁺ is released and this permits the transfer of free hydrated Ni²⁺ ions along with Co²⁺ to the catholyte chamber.

The results do, however, demonstrate that the complexing agent does have a slight selectivity for cobalt ions over nickel in the transport across a single cation exchange membrane and that EDTA used as the disodium salt leads to a slightly better separation than EDTA as the free acid.

The data in (Table 1) show that increasing the EDTA concentration (in the pH range 1.5–2) increases the cobalt selectivity in the catholyte chamber but, that the presence of an excess of EDTA over the stoichiometric required for Ni complexation, does decrease the percentage of both metals transported across the membrane. Increasing the pH to pH 3 leads to a decrease in the transport of both metal ions across the membrane,

Table 1. Effects of EDTA concentration, pH and Co:Ni ratio on the Co and Ni levels in the catholyte chamber using two compartment cell and after 8 h electrolysis time

EDTA/mol dm ⁻³ Co and Ni/mg dm ⁻³		Co mg dm ⁻³ transfer to the catholyte chamber	Ni mg dm ⁻³ transfer to the catholyte chamber	Ratio of Co to Ni in the catholyte chamber	Ratio of Co% to Ni% in the catholyte chamber
Control: in the absence of EDTA	Initial Co and Ni concentration 500 mg dm ⁻³	279	289	0.97:1	0.97:1
EDTA 0.05		264	180	1.5:1	1.5:1
EDTA 0.01		226	96	2.3:1	2.3:1
EDTA 0.025		131	22	5.9:1	5.9:1
EDTA 0.01 (pH 3)		170	87	1.9:1	1.9:1
Co:Ni 500:300 + EDTA 0.06		258	60	4.3:1	2.58
Co:Ni 500:100 + EDTA 0.002		287	24	12:1	2.39
Co:Ni 500:50 + EDTA 0.001		319	16	20:1	1.99

with no significant improvement in the cobalt purification in the catholyte chamber.

The effect of changing the initial Co:Ni ratio was studied for solutions containing Co:Ni mixtures in the ratio 500:300, 500:100 and 500:50 mg dm⁻³ with the corresponding EDTA concentrations being 0.006, 0.002 and 0.001 mol dm⁻³, respectively, to maintain the nickel to EDTA ratio at 0.85:1. The results in Table 1 show that the final purity of the cobalt in the catholyte chamber does depend upon the initial Co:Ni ratio with the degree of purification reducing with increasing nickel content relative to the cobalt.

3.2. Electrodialysis using a three-compartment cell

The results obtained from three compartment cell show a much improved separation compared to the two-compartment cell. In the three-compartment cell the Ni-EDTA complex is transferred through the anion exchange membrane towards the anolyte chamber. Even if EDTA in the anolyte chamber is degraded at the anode surface to release hydrated Ni ions, these hydrated cations cannot penetrate the anion exchange membrane to return to the feed compartment and thence to the catholyte chamber.

When the stoichiometric quantity of EDTA required to complex the nickel ions is used, only the nickel ions will form a complex that will move toward the anode,

leaving the free hydrated cobalt cations to move through the cation exchange membrane towards the cathode. The results (Table 2) show that, in the control experiment, there was no significant separation of nickel from cobalt, but that the addition of EDTA results in a significant selectivity for Co transfer to the catholyte chamber and of Ni to the anolyte chamber.

3.2.1. Effect of changing the concentration of EDTA

The effects of EDTA concentrations (0.005–0.0125 mol dm⁻³) with time on the separation and purification of cobalt in the catholyte chamber are shown in Figure 2 with the 24 h data given in Table 3. The results show that an increase in EDTA concentration enhances the purification of cobalt in the catholyte chamber but reduces the separation efficiency, because it leads to a significant increase in cobalt transportation toward the anolyte chamber along with the nickel. At low EDTA concentrations (0.075 mol dm⁻³ and less) the cobalt purity in the catholyte chamber is low due to the co-transport of some Ni ions but the transfer of cobalt to the anolyte chamber is very low. An increase in the EDTA concentration (0.01 mol dm⁻³ or above) increases the purity of the cobalt in the catholyte chamber but it also leads to an increase in the cobalt transfer to the anolyte chamber with increasing EDTA concentration. A Ni:EDTA ratio of 0.85:1 is found to give a good degree of separation and purification of Co.

Table 2. The effect of EDTA addition on the electrolysis processes of Co–Ni mixture using three compartment cell

Time/h	Cobalt concentration /mg dm ⁻³			Nickel concentration /mg dm ⁻³			Purification	
	catholyte	middle	anolyte	catholyte	middle	anolyte	catholyte Co:Ni	anolyte Ni:Co
Control in absence of EDTA								
0	0	500	0	0	500	0	–	–
4	131	195	0	139	197	0	0.9:1	0:0
8	340	6	0	360	2	0	0.9:1	0:0
With the addition of EDTA (0.01 mol dm ⁻³)								
0	0	500	0	0	500	0		
4	121	290	16	8	340	91	15.1:1	5.7:1
8	305	50	51.5	12	131	265	25:1	5:1

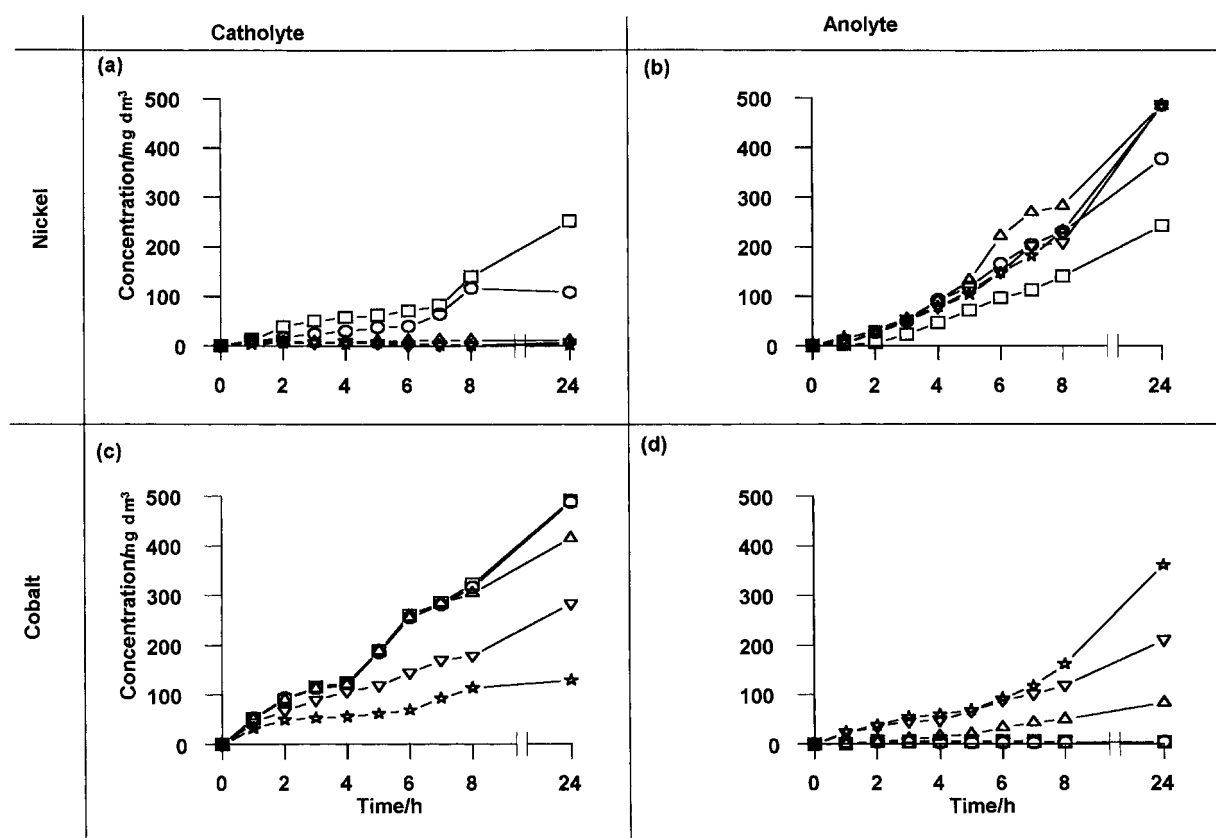


Fig. 2. Effect of EDTA concentration on the Co–Ni separation process using three compartment cell. Concentrations: (□) 0.005, (○) 0.0075, (△) 0.010, (▽) 0.0125 and (☆) 0.016 mol dm⁻³.

3.2.2. HPLC study and the fate of EDTA

The results of studies on the transport and fate of EDTA in the electrodialysis show (Figure 3) that there is a decrease in the EDTA concentration in the feed chamber over time. The greatest decrease occurs during the first 2 h of the reaction. The concentration continues to decrease gradually over the following 22 h to a minimum concentration. The initial HPLC analysis of EDTA shows a major peak at retention time of 6.0 min. During electrodialysis, HPLC analysis of the anolyte chamber solution shows a major peak at retention time of 4.6 min and a broad second peak with a retention time of 7.6 min. The difference in retention time between the major anolyte peak and the original EDTA peak suggests that degradation of EDTA at the anode surface

has taken place and that the degradation product has the lower retention time. The results in (Figure 3), however, show that above 95% mineralization of EDTA present in the anolyte chamber is achieved after 24 h. The function of EDTA in the methodology is to achieve the transfer of nickel complex ions to the anolyte chamber. The anodic destruction of the EDTA in the anolyte chamber ensures that there is no build up of this complexing agent in the feed chamber which would result in additional complex formation with cobalt leading to transfer of more cobalt to the anolyte rather than the catholyte chamber. If the destruction of EDTA was suppressed it would be necessary of use a noncirculating system or to remove the EDTA from the system.

Table 3. Effect of changing the EDTA concentration on the purification and transportation for both Co and Ni using three compartment cell, at current density 8.3 A m⁻² and 0.01 mol dm⁻³ H₂SO₄, after 24 h electrolysis

EDTA/mol dm ⁻³	Ratio of Ni to EDTA	Catholyte chamber			Anolyte chamber		
		/mg dm ⁻³		Ratio of Co to Ni	/mg dm ⁻³		Ratio of Ni to Co
		Co	Ni		Co	Ni	
0.0050	1.5:1	492	254	2:1	4	244	61:1
0.0075	1.13:1	489	109	5.4:1	5	379	63.1
0.0100	0.85:1	416	13	32:1	84	487	6:1
0.0125	0.68:1	285	7	41:1	211	489	2.3:1
0.0150	0.56:1	130	8	16:1	362	486	1.3:1

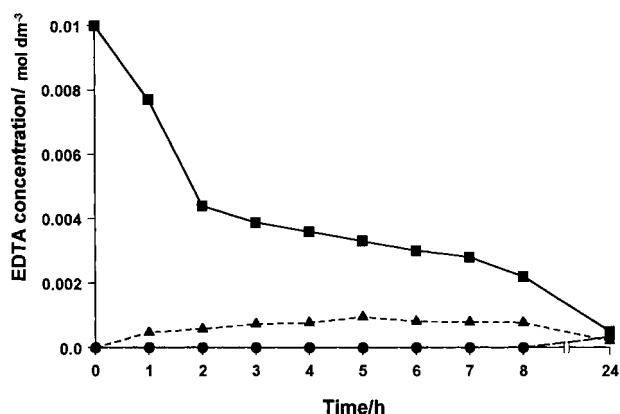


Fig. 3. Determination of the EDTA concentration at (■) feed chamber, (●) catholyte chamber and (▲) anolyte chamber using HPLC system.

The analysis of the catholyte solutions shows that no significant amount of EDTA is transferred from the feed compartment to the catholyte chamber.

3.2.3. Effect of changing the current density

The effect of current density ($8.3\text{--}41.5\text{ A m}^{-2}$) on mass transfer of cobalt and nickel in the electrodialysis process was studied. The results show that increasing the current density leads to only a slight increase in the cobalt purification but gives a small decrease in the cobalt separation efficiency. The cobalt concentration, in the catholyte chamber, was 416 mg dm^{-3} after 24 h at the current density of 8.3 A m^{-2} . The corresponding values at the current density of 20.8 and 41.5 A m^{-2} were 413 and 406 mg dm^{-3} , respectively. The Co:Ni ratio in the catholyte chamber increased from 32:1

to 37:1 at current densities of 8.3 and 41.5 A m^{-2} , respectively.

3.2.4. Effect of changing the cobalt/nickel ratio

The effect of the cobalt:nickel ratio was investigated by: (a) changing the cobalt concentration ($500\text{--}2000\text{ mg dm}^{-3}$), at a constant nickel concentration of (50 mg dm^{-3}) and (b) changing the cobalt concentration ($500\text{--}2000\text{ mg dm}^{-3}$), at a constant nickel concentration of (25 mg dm^{-3}) and a constant EDTA:Ni ratio of 1:0.85.

An increase in the cobalt concentration, reduces the initial transportation of nickel complex toward the anolyte chamber, but after 24 h a complete transfer of the Ni-EDTA complex to the anolyte chamber is achieved. The results in (Tables 4 and 5), show that increasing the cobalt concentration in the feed compartment leads to a slight increase in the cobalt ions entering the anolyte chamber.

3.2.5. Separation of nickel from cobalt using different complexing agents

The electrodialysis of Co-Ni mixture in the presence of the complexing citric acid, salicylaldehyde and acetic acid as alternative of EDTA resulted in no separation under the experimental conditions studied.

3.2.6. Effect of changing concentration of H_2SO_4 in the middle chamber

The effect of acid concentration was studied by changing the sulphuric acid concentration in the feed solution, in the range $0.01\text{--}0.05\text{ mol dm}^{-3}$. The data (Table 6) show that an increase in sulphuric acid concentration increases the cobalt purity in the catholyte chamber, but leads to a

Table 4. Effect of changing the initial Co:Ni ratio on the purification and transportation for both Co and Ni to the catholyte and anolyte chamber, respectively, the EDTA concentration 0.001 mol dm^{-3} , the initial nickel concentration 50 mg dm^{-3} and current density 8.3 A m^{-2} , after 24 h electrolysis

Initial Co:Ni / mg dm^{-3}	Catholyte chamber			Anolyte chamber		
	/ mg dm^{-3}		Ratio of Co to Ni	/ mg dm^{-3}		Ratio of Ni to Co
	Co	Ni		Co	Ni	
500:50	482.7	3.2	151:1	17.3	46.3	2.7:1
1000:50	979	6.3	155:1	20.4	43.3	2.1:1
2000:50	1962	6.3	311:1	22.9	43.3	1.9:1

Table 5. Effect of changing the initial Co:Ni ratio on the purification and transportation for both Co and Ni to the catholyte and anolyte chamber, respectively, the EDTA concentration $0.0005\text{ mol dm}^{-3}$, the initial nickel concentration 25 mg dm^{-3} and current density 8.3 A m^{-2} , after 24 h electrolysis

Initial Co:Ni / mg dm^{-3}	Catholyte chamber			Anolyte chamber		
	/ mg dm^{-3}		Ratio of Co to Ni	/ mg dm^{-3}		Ratio of Ni to Co
	Co	Ni		Co	Ni	
500:25	489.8	0.8	612:1	8.2	24	2.9:1
1000:25	991.6	1.5	661:1	8.4	23.1	2.7:1
2000:25	1983	1.6	1239:1	9	22.3	2.4:1

Table 6. The effect of H_2SO_4 on the purification and transportation for both Co and Ni to the catholyte and anolyte chamber, respectively, the EDTA concentration 0.01 mol dm^{-3} and current density 8.3 A m^{-2} , after 24 h electrolysis

H_2SO_4 /mg dm^{-3}	Catholyte chamber			Anolyte chamber		
	/mg dm^{-3}		Ratio of Co to Ni	/mg dm^{-3}		Ratio of Ni to Co
	Co	Ni		Co	Ni	
0.01	416	13	32:1	84	487	5.7:1
0.02	412	2	206:1	85	494	5.7:1
0.03	405	0	∞	86	500	5.8:1
0.05	410	0	∞	85	500	5.9:1

decrease in the initial transportation of the cobalt and nickel ions toward the catholyte and the anolyte chambers, respectively (Figure 4). The initial decrease in metal ion transfer arised because of the preferential transport of hydrogen and sulphate ions across the cation and anion exchange membranes, respectively, which reduces the initial transport of larger ions (the free hydrated metals ions and anionic metal complexes) across the membranes. This effect was observed by the change in the pH of the feed solution during the electrodialysis processes and the pH changed from 1.1 to 3.1 after 24 h. Increasing the acid concentration results in a slight decrease in the total nickel transferred to the catholyte chamber and gives a significant increase in the cobalt purity.

3.2.7. Effect of other metal impurities

The fate of any other metal (M) impurities on the Ni–Co system will depend upon the stability constants of the

Ni–EDTA and M–EDTA complexes. If the stability constant is similar to nickel or more then there will be competition between the migration of Ni–EDTA and M–EDTA complexes towards the anolyte chamber. In this case the separation can be optimized by changing the EDTA concentration in the feed solution. If the M–EDTA complex is similar to Co–EDTA complex then the metal impurity will have no effect on the separation of nickel from the cobalt in the mixture but only on the levels of impurity metals transferred with the Co.

4. Summary

The results obtained show separation of nickel ions from cobalt sulphate solution can be achieved in the presence of an EDTA as a complexing agent using a

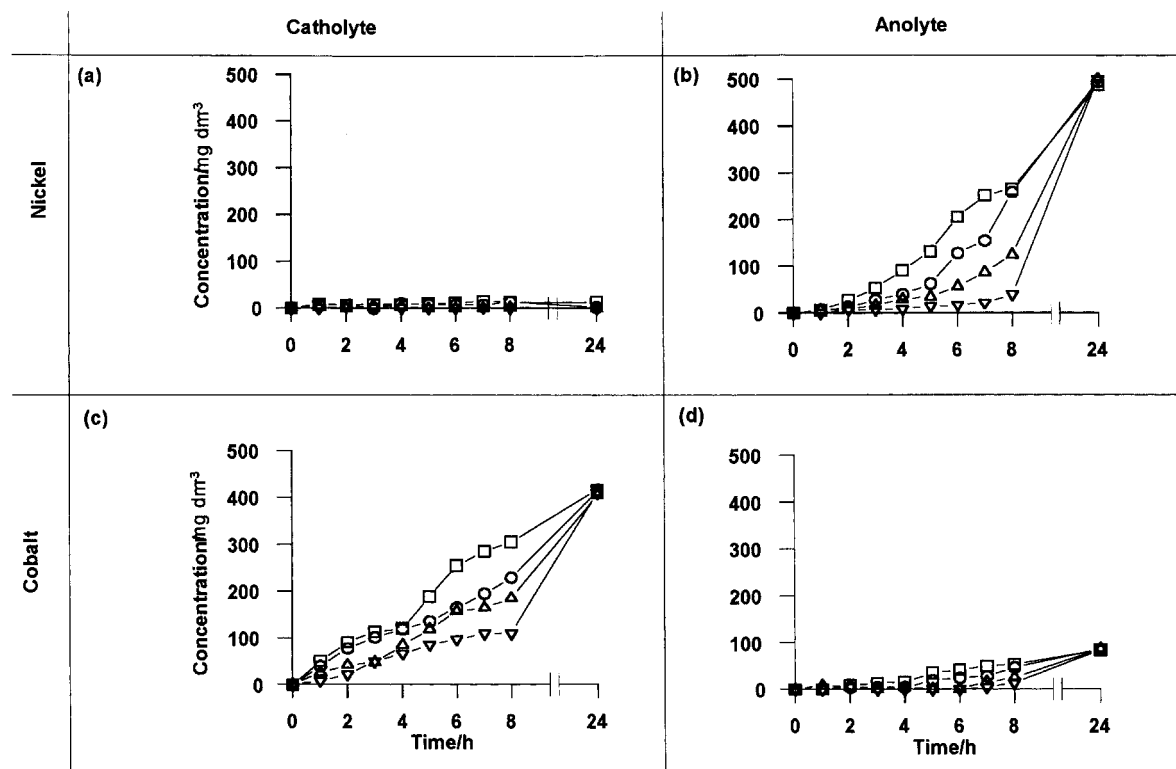


Fig. 4. Effect of H_2SO_4 concentration on separation of nickel–cobalt mixture using a three compartment electrodialysis cell. Concentrations: (\square) 0.01, (\circ) 0.02, (\triangle) 0.03 and (∇) 0.05 mol dm^{-3} .

three compartment electrodialysis cell. The transfer and the fate of EDTA in the cells shows that EDTA transferred to the anolyte as a metal complex and is destroyed on the anode surface to release the hydrated Ni ions but that these ions can not cross the anion exchange membrane to return to the feed or catholyte compartments. In the catholyte chamber most of the cobalt ions will remain in solution but the metal can be deposited on the cathode by increasing the pH to 4–4.5. Data obtained by performing replicate experiments show a good reproducibility with a standard deviation of $\pm 1\%$. The optimum conditions for complete removal of Ni from cobalt sulphate solutions are (a) an EDTA:Ni mole ratio of 1:0.85, (b) a sulphuric acid concentration of $0.03\text{--}0.05\text{ mol dm}^{-3}$ in the feed chamber and (c) a current density of 41.5 A m^{-2} and giving sufficient time to complete the electrodialysis separation.

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